PHYSICAL REVIEW A VOLUME 16, NUMBER 5 NOVEMBER 1977

Maxwell relaxation time for the transverse mode in simple liquids*

Ravinder Bansal

Iwan N. Stranski Institut für Physikalische und Theoretische Chemie, Technische Universität Berlin, Ernst-Reuter-Platz-7, 1000 Berlin-10, West Germany
and Institut für Theoretische Physik, Freie Universität Berlin, Arnimalle 3, 1000 Berlin-33, West Germany

(Received 23 February 1977)

A microscopic expression for the Maxwell relaxation time for the transverse mode in simple liquids has been derived on the basis of the generalized Langevin equation developed by Mori. For this, it is assumed that the correlation function of the second random force is a function of t^2. The derived expression does not involve any adjustable parameter and leads to a correct result for the shear-viscosity coefficient. Numerical predictions for the relaxation time in liquid argon are compared with other existing estimates. It is found that the present results are comparatively much better than some other existing estimates.

I. INTRODUCTION

In our recent papers,[1,2] we have discussed the longitudinal mode of the liquid and derived a microscopic expression for the Maxwell relaxation time for the longitudinal mode $\tau_l(q)$. Numerical predictions of our results for $\tau_l(q)$ in liquid argon were compared with other existing estimates.[3-6] Very good agreement with the experimental observations[7,8] was achieved, which indicated the importance of higher moment relations involved in the expression for $\tau_l(q)$.

This paper is devoted to the study of the transverse mode which describes the shear motion. Study of transverse mode is important because this mode is the main feature which distinguishes the dynamical behavior of the liquid from the solid. Formation of these modes in simple liquids has frequently been investigated in the last few years.[6,8-12] Information about this mode can be obtained only through light-scattering experiments or through computer molecular-dynamics experiments. Neutron-scattering experiments cannot provide any information about the transverse mode as neutrons can couple only to density fluctuations. A molecular-dynamics study of transverse modes in simple liquids, made by Rahman[13] and Levesque *et al.*,[12] greatly facilitates attempts at its theoretical understanding.

Some authors[6,8,9,12,14] did attempt to describe the transverse correlations in simple liquids on the basis of the generalized Langevin equation. But so far no attempt has been made to calculate the relaxation time $\tau_t(q)$ from first principles. Ailawadi *et al.*[8] and Levesque *et al.*[12] determined $\tau_t(q)$ through a least-squares-fit method. Chung and Yip (CY)[9] assumed a simple form for $\tau_t(q)$ which reproduced correctly the small and large q limits of the transverse-current correlation function $C_t(q,\omega)$. Akcasu and Daniels (AD)[6] proposed an expression for $\tau_t(q)$ by requiring $\tau_t(q)$ to yield correct shear viscosity and also that as $q\to\infty$, the peak frequency $(\omega_t)_{\max}$ of $C_t(q,\omega)$ should vanish like the free-particle result. Moreover, their result involved an adjustable parameter. Furthermore, Murase[14] also claims to have derived an expression for $\tau_t(q)$ and compares his results with those of AD. As we discuss in the text, his formulation is different from AD and ours. Apart from this, his expression for $\tau_t(q)$ involves the fourth-moment relation of $C_t(q,\omega)$ for which he used an incomplete expression. All the discrepancies and difficulties mentioned above are hopefully surmounted in the present work.

Our formulation is exactly the same as that of CY or AD, except that we do not assume any specific form for $\tau_t(q)$, but rather determine it under two assumptions. The first assumption is that the correlation time of the first random force is large compared to that of the second random force. The second assumption is that the decay of the second random force is governed by a function of t^2. The resultant expression for $\tau_t(q)$ involves the frequency moments of $C_t(q,\omega)$ up to the sixth, the highest frequency moment hitherto obtained.[15] The constant of proportionality appearing in the expression for $\tau_t(q)$ is determined by requiring that $\tau_t(q)$ reduces to its long-wavelength limit; i.e., it gives the correct shear-viscosity coefficient.

To outline the paper, the theory and calculation of $\tau_t(q)$ are described in Sec. II. Numerical estimates, comparison with the results of other authors, and discussion of results are presented in Sec. III. A brief summary of the present work together with the achievements, limitations, and possible improvements presented in Sec. IV, concludes this paper.

II. FORMULATION

The transverse-current correlation function is defined as

$$C_t(q,t)=q^2\left\langle\sum_{i=1}^{N} v_i^x(t)e^{-iqy_i(t)}\sum_{j=1}^{N} v_j^x(0)e^{-iqy_j(0)}\right\rangle , \qquad (1)$$

where $\vec{q}$ is along the y axis. Let us introduce the Laplace transform

$$\tilde{C}_t(q,p)=\int_0^\infty dt\, C_t(q,t)e^{-pt} , \qquad (2)$$

p being the Laplace variable. In Mori's[16] memory-function formalism, the time-correlation function $C_t(q,t)$ satisfies an integro-differential equation of the form

$$\frac{dC_t(q,t)}{dt}=-\int_0^t dt' M_1(q,t-t')C_t(q,t') , \qquad (3)$$

where the kernel $M_1(q,t)$ is the correlation function of first random forces and is known as the memory function or damping function associated with $C_t(q,t)$. $M_1(q,t)$ also satisfies an equation akin to (3) with a "higher-order" memory function $M_2(q,t)$ as the kernel and so on. In terms of Laplace transforms, this chain of equations can be written

$$\tilde{C}_t(q,p)=\frac{C_t(q,0)}{p+\tilde{M}_1(q,p)} , \quad \tilde{M}_k(q,p)=\frac{\delta_{kt}}{p+\tilde{M}_{k+1}(q,p)} \qquad (4)$$

where $\delta_{kt}=M_k(q,t=0)$ and are expressible in terms of the moments of $C_t(q,\omega)$. Explicit expressions for the first three δ_t are given below:

$$\begin{aligned}&\delta_{1t}=\langle\omega_t^2\rangle ,\\ &\delta_{1t}(\delta_{1t}+\delta_{2t})=\langle\omega_t^4\rangle ,\\ &\delta_{1t}[\delta_{2t}\delta_{3t}+(\delta_{1t}+\delta_{2t})^2]=\langle\omega_t^6\rangle ,\end{aligned} \qquad (5)$$

where the nth frequency moment of $C_t(q,\omega)$ is defined by the relation

$$\langle\omega_t^n\rangle=\int_{-\infty}^{\infty} d\omega\, \omega^n C_t(q,\omega)/C_t(q,t=0) . \qquad (6)$$

In an earlier paper,[15] we extended the calculation of frequency-moment sum rules of $C_t(q,\omega)$ up to the sixth order. In another paper,[1] we simplified the expressions for these higher-order moment sum rules by performing various angular integrations involved in the two-body and three-body integrals which appear in these moment relations.

In order to determine $C_t(q,\omega)$, it is necessary to truncate the hierarchy of Eqs. (4) at some suitable stage. We truncate it at the second stage by assuming that $M_2(q,t)$ decays much faster than $M_1(q,t)$ and obtain

$$\tilde{C}_t(q,p)=\frac{C_t(q,t=0)}{p+\tilde{M}_1(q,p)} , \qquad (7)$$

where $C_t(q,t=0)=q^2k_BT/m$. k_B is the Boltzmann constant and T is the absolute temperature. From (7), it is easy to write an expression for $C_t(q,\omega)$ which is equal to π^{-1} times the real part of $\tilde{C}_t(q,p)$. This gives

$$\frac{\pi C_t(q,\omega)}{C_t(q,t=0)}=\frac{M_1'(q,\omega)}{[M_1'(q,\omega)]^2+[\omega-M_1''(q,\omega)]^2} , \qquad (8)$$

$M_1'(q,\omega)$ and $M_2''(q,\omega)$ being the real and imaginary parts of $\tilde{M}_1(q,i\omega)$.

The next step is to evaluate the memory function $M_1(q,t)$ for which we write its equation of motion

$$\frac{dM_1(q,t)}{dt}=-\int_0^t dt' M_2(q,t-t')M_1(q,t') . \qquad (9)$$

The truncation scheme mentioned above in Eq. (7) allows us to rewrite Eq. (9) as

$$\frac{dM_1(q,t)}{dt}=-\tau_t^{-1}(q)M_1(q,t) , \qquad (10)$$

with

$$\tau_t^{-1}(q)=\int_0^\infty dt\, M_2(q,t)=\tilde{M}_2(q,0) . \qquad (11)$$

This is the Maxwell approximation for the time correlation of the first random force and $\tau_t(q)$ is the Maxwell relaxation time. Equation (10) results because the mentioned approximation implies that the correlation function $M_2(q,t-t')$ will make a maximum contribution only when $t\simeq t'$, and in such a time interval the correlation function $M_2(q,t')$ is nearly a constant and can be set equal to $M_2(q,t)$. Then the solution of (10) can be readily seen to be the following exponential:

$$M_1(q,t)=\delta_{1t}(q)e^{-t/\tau_t(q)} . \qquad (12)$$

Substitution of (12) into (8) shows that the resultant expression for $C_t(q,\omega)$ will give correct zeroth and second frequency moments irrespective of the choice of $\tau_t(q)$. The problem is now reduced to the calculation of the relaxation time $\tau_t(q)$.

As a first approximation, it seems more reasonable to estimate the integral of Eq. (11) from the short-time behavior of $M_2(q,t)$:

$$M_2(q,t)=\delta_{2t}(1-\tfrac{1}{2}\delta_{3t}t^2+\cdots) . \qquad (13)$$

Assuming $M_2(q,t)$ to be a function of $\delta_{3t}t^2$ yields

$$\tau_t^{-1}(q)\propto\delta_{2t}/(\delta_{3t})^{1/2} . \qquad (14)$$

The constant of proportionality is denoted by ξ and depends on the function used to model the higher-order terms in the expansion of $M_2(q,t)$. Thus Eq. (14) can be written as

$$\tau_t^{-1}(q)=\xi\delta_{2t}/(\delta_{3t})^{1/2} . \qquad (15)$$

The corresponding approximate form for $C_t(q,t)$ would be

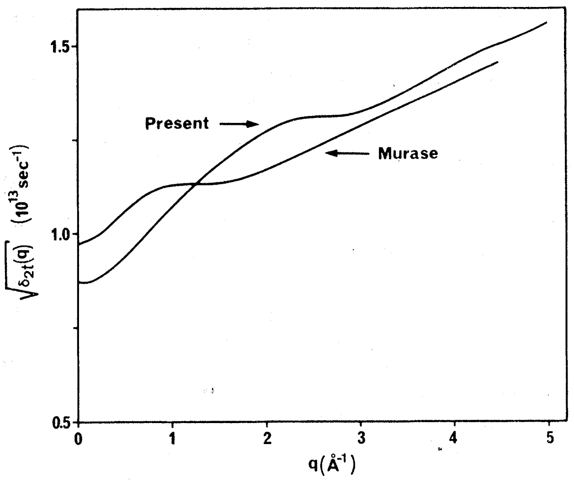

FIG. 1. Wave-number dependence of $(\delta_{2t})^{1/2}$.

$$C_t(q,t)=\frac{q^2k_BT}{m}\exp\left(\frac{-t}{2\tau_t(q)}\right)\left(\cos(\epsilon t)+\frac{\sin(\epsilon t)}{2\epsilon\tau_t(q)}\right),$$

with

$$\epsilon^2=\delta_{1t}[1-(\xi/2)^2]. \tag{16}$$

We determine the constant of proportionality ξ by requiring $C_t(q,\omega)$ to reproduce the correct Kubo limit:

$$\lim_{\omega\to 0}\lim_{q\to 0}\frac{\omega^2}{q^2}C_t(q,\omega)=\frac{k_BT}{\pi m^2\rho}\eta. \tag{17}$$

ρ is the number density and η is the shear-viscosity coefficient. We then find that

$$\xi=\frac{m\rho}{\eta}\lim_{q\to 0}\frac{\delta_{1t}}{q^2}\frac{(\delta_{3t})^{1/2}}{\delta_{2t}}. \tag{18}$$

Here it is worth pointing out that our approach is different from Murase,[14] who assumes a Gaussian decay for $M_1(q,t)$:

$$M_1(q,t)=\delta_{1t}\exp(-t^2\delta_{2t}/2), \tag{19}$$

which is different from our expression for $M_1(q,t)$, an exponential. Furthermore, Murase defines the relaxation time as the time in which $M_1(q,t)$ decays by $1/e$ and obtains

$$\tau_t(q)=(2/\delta_{2t})^{1/2}. \tag{20}$$

Thus this relaxation time corresponds to a Gaussian form for the memory function $M_1(q,t)$. It is, therefore, inconsistent to compare the results of (20) with the model of AD.

III. RESULTS AND DISCUSSION

We turn now to the numerical calculation of the relaxation time discussed in the preceding section. We consider only one thermodynamic state ($m\rho$ $=1.407$ g/cm^3, $T=76$ °K) corresponding to liquid argon near to its triple point. The numerical results for the wave-number dependence of the various frequency moments, to be used here as input, were presented and discussed in Ref. 1. The reader is, therefore, referred to that paper for details.

In Fig. 1, we have compared the results of our calculation for the quantity $(\delta_{2t})^{1/2}$ with those obtained by Murase.[14] This comparison is made in order to make clear a characteristic difference introduced by using a complete expression for $\langle\omega_t^4\rangle$ and the Kirkwood superposition approximation for $g_3(\vec{r},\vec{r}')$ (the triplet correlation function) needed to evaluate $\langle\omega_t^4\rangle$. Murase has erroneously estimated $\langle\omega_t^4\rangle$ because he missed the *sine* term and also used a low-order decoupling approximation for three-body terms involved in $\langle\omega_t^4\rangle$. Now the q dependence of $(\delta_{2t})^{1/2}$ is not much different from the relaxation time estimated by AD. Of course, as pointed out earlier, it is not consistent to compare the relaxation time obtained by Murase with that of AD.

In Fig. 2, we have depicted the wave-number dependence of the inverse relaxation time $\tau_t^{-1}(q)$. The solid and open circles are, respectively, the results obtained by Ailawadi *et al.*[8] and Levesque *et al.*[12] by least-squares fitting the expression (8) to the molecular-dynamics data. Ailawadi *et al.* fitted the data obtained by Rahman,[13] whereas Levesque *et al.* fitted their own data. Also shown in Fig. 2 is the curve obtained from the model of AD, who assumed that

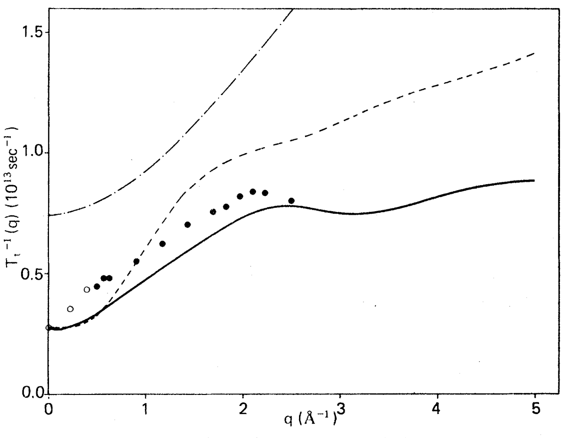

FIG. 2. Wave-number dependence of the inverse relaxation time $\tau_t^{-1}(q)$. Solid circles, results obtained by Ailawadi *et al.* (Ref. 8) by fitting Eq. (8) to the molecular-dynamics data of Rahman (Ref. 13); open circles, results obtained by Levesque *et al.* (Ref. 12) by fitting Eq. (8) to their own data; dashed curve, obtained from the expression proposed by AD[6]; dash-dot curve, obtained from the expression proposed by CY[9]; and full curve, the results of the present calculation.

$$\tau_t^{-2}(q) = 2\delta_{1t}^2 + [\tau_t^{-2}(0) + (qv_0)^2 - 2\delta_{1t}](1 + q^2 q_0^{-2})^{-1}, \tag{21}$$

where

$$\tau_t^{-1}(0) = \frac{m\rho}{\eta} \lim_{q\to 0} \frac{\delta_{1t}}{q^2}, \tag{22}$$

and $v_0 = (2k_BT/m)^{1/2}$ is the thermal speed of the particles. They adjusted the parameter $q_0 = 1.5$ Å^{-1} by fitting Rahman's molecular-dynamics data. Their results are shown by the dashed curve.

Chung and Yip (CY) have approximated $\tau_t(q)$ in a rather crude manner. In order to analyze Rahman's data for $q \leqslant 1$ Å^{-1}, they replaced $\tau_t(q)$ simply by its limiting value $\tau_t(0)$. For $q > 1$ Å^{-1}, they proposed that

$$\tau_t^{-2}(q) = \tau_t^{-2}(0) + (qv_0)^2, \tag{23}$$

which should correctly reproduce both the small- and large-q limits. But for $\tau_t(0)$, needed in (23), they used the value calculated from the expression

$$\tau_t^2(q) = \frac{\pi}{2} \frac{\langle \omega_t^2(q)\rangle}{\langle \omega_t^4(q)\rangle - \langle \omega_t^2(q)\rangle^2}. \tag{24}$$

This expression results if one assumes a Gaussian decay for the memory function $M_1(q, t)$. So they are obviously inconsistent in choosing $\tau_t(0)$. Results of Eq. (23) with $\tau_t(0) = 0.135 \times 10^{-12}$ sec are also shown in Fig. 2.

CY also attempted to determine $\tau_t^{-1}(q)$ by examining the frequency where the observed $C_t(q, \omega)$ has a peak. This peak position is denoted by $(\omega_t)_{\max}$, and physically this corresponds to the phenomenon of shear-wave propagation in the liquid. Then they calculated $\tau_t(q)$ from the expression

$$\tau_t^{-2}(q) = 2[\langle \omega_t^2\rangle - (\omega_t)_{\max}^2], \tag{25}$$

which can be obtained from Eq. (8). Since we do not have access to Rahman's original data for $C_t(q, \omega)$, we cannot compare the results of approximation (25) with our results. Also, we cannot compare the results for spectral densities. However, comparison of our results for $\tau_t(q)$ with various prescriptions for $\tau_t(q)$ described above should definitely be instructive as to the usefulness of our results.

For smaller wave numbers ($q \leqslant 0.5$ Å^{-1}), our results are similar to those of AD. This is because expression (21) and our result for $\tau_t(q)$ reproduce the shear-viscosity correctly. Furthermore, our results seem to be in phase with the observed results. On the other hand, results of AD tend to increase rapidly after $q \sim 0.5$ Å^{-1} and cross the observed results and seem to differ in their q dependence. The results of CY are considerably higher in magnitude.

IV. SUMMARY

We have presented a simple prescription for calculating the Maxwell relaxation time for the transverse mode in simple liquids in terms of the frequency moments of the spectral function of the transverse-current correlation function. Numerical estimates of our result for $\tau_t(q)$ in liquid argon are found to be consistently slightly below the observed results. However, the q dependence of $\tau_t(q)$ calculated by us is much improved over the results of other authors and is in phase with the observed results. The consistent difference of our results from the observed ones can be partially ascribed to our use of the superposition approximation for the triplet correlation function and the decoupling approximation used for evaluating four-body integrals appearing in sixth frequency moment of $C_t(q, \omega)$. At present, we do not know the errors involved due to the use of mentioned approximations for higher-order static correlation functions. However, it should be expected that use of better approximations for these higher-order correlation functions should improve the results for $\tau_t(q)$. In any case, we believe that the wave-number dependence of our results is encouraging enough to make the calculation worthwhile.

ACKNOWLEDGMENTS

I wish to express my sincere thanks to Professor K. N. Pathak for his interest in the present work. Thanks are due to Dr. N. K. Ailawadi for several helpful discussions and encouragement. I am also grateful to Professor W. Bruns for the hospitality provided by him in the Iwan N. Stranski Institute of the Technical University of Berlin.

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*Work supported by the Deutsche Forschungsgemeinschaft.

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